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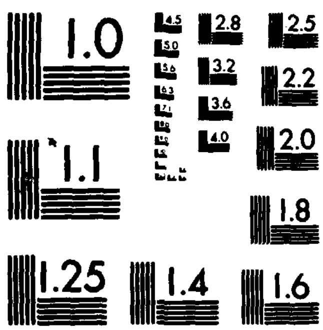

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Calculation on Optical Effect of Matter from First Principles Using Group Theoretical Techniques (U)

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1. INTRODUCTION.

Scattering of light by molecules is commonly dealt with through Rayleigh-Debye theory.[1-3] Such approach is known to be applicable to molecules whose effective index of refraction is close to unity and to imply a number of approximations which may have rather severe effects.[3,4] In this paper we face the problem by adapting the method devised by Johnson,[5] and successfully used to calculate the electronic states of large molecules,[6,7] to the scattering of electromagnetic waves. Accordingly, we model a molecule as a cluster of spherical scatterers, possibly of different radii and refractive indexes. A plane electromagnetic wave, incident to the cluster, undergoes multiple scatterings which we account for by expanding the scattered wave in a multicentered series of vector harmonics. The expansion coefficients turn out to be the solutions of the system of linear equations obtained by expanding both the incident field and that within the spheres in a series of vector harmonics, and imposing the boundary conditions across the surface. Due to the presence of the incident plane wave, the above system is nonhomogeneous.[8]

The method outlined above does not require any approximation, except for the truncations of the expansions in vector harmonics, in order to get a system of finite order. For large clusters and for convergency reasons, however, one might have to solve rather large systems. Anyway, if the cluster possesses symmetry properties, as is the case for actual molecules, one can use group theoretical techniques to get the system in factorized form. By expanding both the incident and the scattered field in symmetry-adapted combinations of vector harmonics, indeed, the system factorizes in much the same way as quantum mechanical secular equations,[9] except that the inhomogeneous terms are not independent of the row index of the multidimensional irreducible representations. As a consequence, we have to solve all the systems arising out of the factorization procedure. It will become apparent,

however, that this peculiarity of the present problem does not cancel the undoubted advantages of the group theoretical techniques.

2. MULTIPOLAR EXPANSION OF THE FIELD.

The cluster whose scattering properties we want to study is composed of N non-magnetic spheres whose centers lie at $\mathbf{R}_\alpha$ and whose radii and (possibly complex) refractve indices are b_α and n_α, respectively. We refer the cluster to a fixed set of axes and choose the direction of incidence of the incoming plane wave through direction cosines of its wavevector. A straightforward calculation along the lines sketched by Jackson[10] allows us to write the field of a circularly polarized plane wave of wavevector $\mathbf{k}$ as

$$\mathbf{E}^{(i)}_{\eta} = \sum_{LM} W_{\eta LM}(\hat{\mathbf{k}})[j_L(kr)\mathbf{X}_{LM}(\hat{\mathbf{r}}) + \eta\frac{1}{k}\nabla\times j_L(kr)\mathbf{X}_{LM}(\hat{\mathbf{r}})] \qquad (2\text{-}1a)$$

$$i\mathbf{B}^{(i)}_{\eta} = \eta\mathbf{E}^{(i)}_{\eta} \qquad (2\text{-}1b)$$

with $\eta = \pm 1$ according to the polarization and

$$W_{\eta LM}(\hat{\mathbf{k}})^{*} = 4\pi i^{L}(\mathbf{e}_1 + i\eta\mathbf{e}_2)\cdot\mathbf{X}^{*}_{LM}(\hat{\mathbf{k}}) \qquad (2\text{-}2)$$

where $\mathbf{e}_1$ and $\mathbf{e}_2$ are unit vectors orthogonal to $\mathbf{k}$ and to each other. In the above equations the vector spherical harmonics, $\mathbf{X}_{LM}$, are defined according to Jackson.[10]

The field scattered by the cluster is expanded in a multicentered series of multipoles including only outgoing spherical waves at infinity:

$$\mathbf{E}^{(s)}_{\eta} = \sum_{\alpha}\sum_{LM}[A^{\alpha}_{\eta LM}h_L(kr_\alpha)\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha) + B^{\alpha}_{\eta LM}\frac{1}{k}\nabla\times h_L(kr_\alpha)\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha)] \qquad (2\text{-}3a)$$

$$i\mathbf{B}^{(s)}_{\eta} = \sum_{\alpha}\sum_{LM}[B^{\alpha}_{\eta LM}h_L(kr_\alpha)\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha) + A^{\alpha}_{\eta LM}\frac{1}{k}\nabla\times h_L(kr_\alpha)\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha)] \qquad (2\text{-}3b)$$

with $\mathbf{r}_\alpha = \mathbf{r} - \mathbf{R}_\alpha$. The superscript(1) on the spherical Hankel functions of the first kind will be omitted throughout for simplicity. As regards the field within the spheres we remark that the present theory is not restricted to homogeneous spheres, provided the n_α's are spherically symmetric. Therefore, within the α - th sphere we can write[11]

$$\mathbf{E}^{(t)\alpha}_{\eta} = \sum_{LM}[C^{\alpha}_{\eta LM}R^{\alpha}_{L}(r_\alpha)\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha) + \frac{1}{n_\alpha^2}D^{\alpha}_{\eta LM}\frac{1}{k}\nabla\times S^{\alpha}_{L}(r_\alpha)\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha)] \qquad (2\text{-}4a)$$

$$i\mathbf{B}^{(t)\alpha}_{\eta} = \sum_{LM}[D^{\alpha}_{\eta LM}S^{\alpha}_{L}(r_\alpha)\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha) + C^{\alpha}_{\eta LM}\frac{1}{k}\nabla\times R^{\alpha}_{L}(r_\alpha)\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha)] \qquad (2\text{-}4b)$$

where R_L^α and S_L^α are the solutions, regular at $r_\alpha = 0$, of the equations

$$\left[\frac{d^2}{dr_\alpha^2} - \frac{L(L+1)}{r_\alpha^2} + k^2 n_\alpha^2\right](r_\alpha R_L^\alpha) = 0 \qquad (2\text{-}5a)$$

and

$$\left[\frac{d^2}{dr_\alpha^2} - \frac{2}{r_\alpha n_\alpha}\frac{dn_\alpha}{dr_\alpha}\frac{d}{dr_\alpha} - \frac{L(L+1)}{r_\alpha^2} + k^2 n_\alpha^2\right](r_\alpha S_L^\alpha) = 0 \qquad (2\text{-}5b)$$

respectively. Of course, for uniform n_α's, $R_L^\alpha(r_\alpha) \equiv S_L^\alpha(r_\alpha) \equiv j_L(K_\alpha r_\alpha)$ with $K_\alpha = kn_\alpha$.

3. SYMMETRY ADAPTED MULTIPOLAR EXPANSION OF THE FIELD

The expansion coefficients in equations (2-3) and (2-4) are solutions of the system of linear nonhomogeneous equations obtained by imposing on $\underset{\sim}{E}$ and $\underset{\sim}{B}$ the customary boundary conditions at the surface of each one of the spheres. However, by first exploiting the symmetry properties of the cluster and thus putting equations (2-1) and (2-3) in symmetry-adapted form, we shall get the above system in factorized form.

First of all we partition the cluster into sets of spheres which are transformed into each other by the symmetry operations. This does not imply renumbering of the spheres but only association of each site index, α, to the appropriate set index, σ. Then we construct symmetrized combinations out of the vector harmonics centered at the sites of each set. To this end we remark that if $f_L(kr)$ is a spherical Bessel or Hankel function then

$$f_L(kr)\underset{\sim}{X}_{LM}(\hat{r}) = -f_L(k\hat{r})\underset{\sim}{T}^M_{LL}(\hat{r}) \qquad (3\text{-}1a)$$

$$\nabla\times f_L(kr)\underset{\sim}{X}_{LM}(\hat{r}) = -ik\left[\sqrt{\frac{L+1}{2L+1}}f_{L+1}\underset{\sim}{T}^M_{LL+1} - \sqrt{\frac{L+1}{2L+1}}f_{L-1}\ \underset{\sim}{T}^M_{LL-1}\right] \qquad 3\text{-}1b)$$

the $\underset{\sim}{T}$'s being irreducible spherical tensors.[12] Therefore, both the magnetic and the electric 2^L-pole fields transform according to the representation $D^{(L)}$ of the full rotation group.[12,13,27] Accordingly, let S be a symmetry operation such that

$$S\underset{\sim}{R}_\alpha = \underset{\sim}{R}_\beta$$

with α and β in the same set, of course, and let O_s be the associated operator, then[14] if S is a proper rotation

$$O_s f_L(kr_\alpha)\underset{\sim}{X}_{LM}(\hat{r}_\alpha) = f_L(kr_\beta)\sum_{M'} D^{(L)}_{M'M}(S)\underset{\sim}{X}_{LM'}(\hat{r}_\beta) \qquad (3\text{-}2a)$$

$$O_s\nabla\times f_L(kr_\alpha)\underset{\sim}{X}_{LM}(\hat{r}_\alpha) = \sum_{M'}\nabla\times f_L(kr_\beta)D^{(L)}_{M'M}(S)\underset{\sim}{X}_{LM'}(\hat{r}_\beta). \qquad (3\text{-}2b)$$

However, if S is an improper rotation one must take into account that the parity of $f_L \underset{\sim}{X}_{LM}$ is $(-)^L$ while that of $\nabla \times f_L \underset{\sim}{X}_{LM}$ is $(-)^{L+1}$. Therefore for improper rotations, the right-hand side of equation of (3-2a) must be multiplied by $(-)^L$ and the right-hand side of equation (3-2b) by $(-)^{L+1}$ and the argument in $D^{(L)}_{M'M}$ must be understood as the proper rotational part of S. As a consequence, if the symmetry group of the cluster also includes harmonics belonging to the rows of the ν-th irreducible representation, one has to apply the projection operators[15,16]

$$P^{\nu}_{pq} = \frac{g_\nu}{g} \sum_s D^{(\nu)*}_{pq}(S) O_s \tag{3-3}$$

both to the magnetic and the electric 2^L poles. Thus we can write

$$\underset{\sim}{H}^{\nu p \sigma}_{NL} = \sum_{\alpha \in \sigma} \sum_{M \in N} a^{\nu p \alpha}_{NLM} h_L(kr_\alpha) \underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}_\alpha) \tag{3-4a}$$

$$\underset{\sim}{K}^{\nu p \sigma}_{N'L} = \sum_{\alpha \in \sigma} \sum_{\bar{M} \in N'} b^{\nu p \alpha}_{N'L\bar{M}} \frac{1}{k} \nabla \times h_L(kr_\alpha) \underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}_\alpha) \tag{3-4b}$$

for the combinations of magnetic and electric 2^L poles, respectively, centered at the sites of the σ-th set. The superscripts ν, p indicate that the combination belongs to the p-th row of the ν-th irreducible representation and the index N recalls, when appropriate, that one can get more than one set of basis functions for a given L. The scattered field can thus be written in symmetrized form as

$$\underset{\sim}{E}^{S}_{\eta} = \sum_{\nu p} \sum_{\sigma L} \left[\sum_N A^{\nu p \sigma}_{\eta N L} \underset{\sim}{H}^{\nu p \sigma}_{NL} + \sum_{N'} B^{\nu p \sigma}_{\eta N' L} \underset{\sim}{K}^{\nu p \sigma}_{N'L} \right] \tag{3-5a}$$

the corresponding expression for $i\underset{\sim}{B}^{(s)}_{\eta}$ being obtained through the Maxwell equation $i\underset{\sim}{B} = \frac{1}{k} \nabla \times \underset{\sim}{E}$; the index η denotes the polarization as in the preceding section.
Comparison of equation (3-5) with equation (2-3) shows that

$$\sum_{\nu p} \sum_N A^{\nu p \sigma}_{\eta N L} a^{\nu p \alpha}_{NLM} = A^{\alpha}_{\eta LM} \quad , \quad \sum_{\nu p} \sum_N B^{\nu p \sigma}_{\eta N L} b^{\nu p \alpha}_{NLM} = B^{\alpha}_{\eta LM} \tag{3-6}$$

Furthermore, since we work with unitary irreducible representations, as shown by the structure of the operators, equation (3-3), the coefficients $a^{\nu p \alpha}_{NLM}$ have the property

$$\sum_{\alpha \in \sigma} \sum_M (a^{\nu p \alpha}_{NLM})^* a^{\nu p \alpha}_{N'LM} = \delta_{NN'} \; , \; \sum_{\alpha \in \sigma} \sum_M (b^{\nu p \alpha}_{NLM})^* b^{\nu p \alpha}_{N'LM} = \delta_{NN'} \tag{3-7}$$

Now we have to decompose the incident field into parts belonging to the rows of irreducible representations of the symmetry group of the cluster. This is easily done for the projection operators, equation (3-3), have the completeness property[15,16]

$$\sum_{\nu}\sum_{p} F_{pp}^{\nu} = 1 \tag{3-8}$$

Thus we can write

$$\begin{aligned} E_n^{(i)} &= \sum_{LM} W_{nLM}(\hat{k}) \sum_{\nu p}\left[F_{pp}^{\nu}\, j_L(kr)X_{LM}(\hat{r}) + n\frac{1}{k}F_{pp}^{\nu}\nabla\times j_L(kr)X_{LM}(\hat{r})\right] \\ &= \sum_{\nu p}\sum_{LM} W_{nLM}(\hat{k})\left[J_{LM}^{\nu p} + nL_{LM}^{\nu p}\right], \end{aligned} \tag{3-9}$$

and an analgous equation for $iB_n^{(i)}$, where

$$\begin{aligned} J_{LM}^{\nu p} &= \frac{g_\nu}{g}\sum_{s} D_{pp}^{(\nu)*}(S)\sum_{M'} D_{M'M}^{(L)}(S) j_L(kr)X_{LM'}(\hat{r}) \\ &= \sum_{M'} c_{LMM'}^{\nu p}\, j_L(kr)X_{LM'}(\hat{r}) \end{aligned}$$

and

$$L_{LM}^{\nu p} = \sum_{M'} c_{LMM'}^{\nu p}\frac{1}{k}\nabla\times j_L(kr)X_{LM'}(\hat{r}).$$

This completes the symmetrization procedure because equation (2-4) need not be symmetrized for reasons that will become clear in the next section.

4. EQUATIONS FOR THE COEFFICIENTS

We are now able to write the equations for the coefficients $A_{nNL}^{\nu p\sigma}$ and $B_{nNL}^{\nu p\sigma}$ of the scattered wave, equation (3-5), by imposing to E and B the appropriate boundary conditions at the surface of each one of the spheres. To this end we rewrite equations (3-5) and (3-9) in terms of vector harmonics centered at a single site, say R_α, through the use of the appropriate addition theorems.[17,18] Indeed, near the surface of the α-th sphere belonging to the σ-th set we have

$$\begin{aligned} E_n^{(s)} = \sum_{\nu p\sigma}\sum_{L}\Bigg\{ & \sum_{N} A_{nNL}^{\nu p\sigma}\sum_{M\in N} a_{NLM}^{\nu p\alpha} h_L(kr_\alpha)X_{LM}(\hat{r}_\alpha) + \sum_{N'} B_{nN'L}^{\nu p\sigma}\sum_{\bar{M}\in N'} b_{N'L\bar{M}}^{\nu p\alpha}\frac{1}{k}\nabla\times h_L(kr_\alpha)X_{L\bar{M}}(\hat{r}_\alpha) \\ & + \sum_{N}\sum_{\tau} A_{nNL}^{\nu p\tau}\sum_{\beta\in\tau}\sum_{M\in N} a_{NLM}^{\nu p\beta}\sum_{L'M'}\left[H_{L'M'LM}^{\alpha\beta}\, j_{L'}(kr_\alpha)X_{L'M'}(\hat{r}_\alpha) + K_{L'M'LM}^{\alpha\beta}\frac{1}{k}\nabla\times j_{L'}(kr_\alpha)X_{L'M'}(\hat{r}_\alpha)\right] \\ & + \sum_{\tau}\sum_{N'} B_{nN'L}^{\nu p\tau}\sum_{\beta\in\tau}\sum_{\bar{M}\in N'} b_{N'L\bar{M}}^{\nu p\beta}\left[K_{L'M'L\bar{M}}^{\alpha\beta}\, j_{L'}(kr_\alpha)X_{L'M'}(\hat{r}_\alpha) + H_{L'M'L\bar{M}}^{\alpha\beta}\frac{1}{k}\nabla\times j_{L'}(kr_\alpha)X_{L'M'}(\hat{r}_\alpha)\right]\Bigg\} \end{aligned} \tag{4-1}$$

$$\begin{aligned} E_n^{(i)} = \sum_{LM} W_{nLM}(\hat{k})\sum_{\nu p}\sum_{M'}\Bigg\{ & c_{LMM'}^{\nu p}\sum_{L''M''}\left[J_{L''M''LM'}^{\alpha}\, j_{L''}(kr_\alpha)X_{L''M''}(\hat{r}_\alpha) + L_{L''M''LM'}^{\alpha}\frac{1}{k}\nabla\times j_{L''}(kr_\alpha)X_{L''M''}(\hat{r}_\alpha)\right] \\ & + n d_{LMM'}^{\nu p}\sum_{L''M''}\left[L_{L''M''LM'}^{\alpha}\, j_{L''}(kr_\alpha)X_{L''M''}(\hat{r}_\alpha) + J_{L''M''LM'}^{\alpha}\frac{1}{k}\nabla\times j_{L''}(kr_\alpha)X_{L''M''}(\hat{r}_\alpha)\right]\Bigg\} \end{aligned} \tag{4-2}$$

and analogous expressions for $i\underset{\sim}{B}_{\eta}^{(s)}$ and $i\underset{\sim}{B}_{\eta}^{(i)}$. In equation (4-1) we define

$$H^{\alpha\beta}_{L'M'LM} = (1-\delta_{\alpha\beta})\sum_{\mu} C(1,L',L';-\mu,M'+\mu)4\pi\sum_{\lambda} i^{L'-L-\lambda} I_{\lambda}(L',M'+\mu;L,M+\mu)$$

$$\times\, h_{\lambda}(kR_{\alpha\beta})Y^{*}_{\lambda M'-M}(\hat{R}_{\alpha\beta})C(1,L,L;-\mu,M+\mu) \tag{4-3a}$$

$$K^{\alpha\beta}_{L'M'LM} = -i\sqrt{\frac{2L'+1}{L'}}\,(1-\delta_{\alpha\beta})\sum_{\mu} C(1,L',L'+1;-\mu,M'+\mu)4\pi\sum_{\lambda} i^{L'-L-\lambda+1}$$

$$\times\, I_{\lambda}(L'+1,M'+\mu;L,M+\mu)h_{\lambda}(kR_{\alpha\beta})Y^{*}_{\lambda M'-M}(\hat{R}_{\alpha\beta})C(1,L,L;-\mu,M+\mu) \tag{4-3b}$$

with $\underset{\sim}{R}_{\alpha\beta} = \underset{\sim}{R}_{\beta} - \underset{\sim}{R}_{\alpha}$, while in equation (4-2) $J^{\alpha}_{L'M'LM}$ and $L^{\alpha}_{L'M'LM}$ are identical to $H^{\alpha\beta}_{L'M'LM}$ and $K^{\alpha\beta}_{L'M'LM}$ respectively but for the substitution of j_{λ} to h_{λ} and $\underset{\sim}{R}_{\beta}=0$. The quantities

$$I_{\lambda}(L'M';LM) = \int Y^{*}_{L'M'}\, Y_{LM} Y_{\lambda M'-M}\, d\Omega$$

are the well-known Gaunt integrals.[19]

Now, taking the dot product of equations (4-1), (4-2) and (2-4) in turn with $\underset{\sim}{r}_{\alpha}\, Y^{*}_{\ell m}(\underset{\sim}{r}_{\alpha})$ and $\underset{\sim}{r}_{\alpha} \times \underset{\sim}{X}^{*}_{\ell m}(\underset{\sim}{r}_{\alpha})$ we get the radial and the tangential components of the field at the surface of the α-th sphere. Imposition of the boundary conditions and integration over the angles yields, for each ℓ, m six equations among which the coefficients of the internal field, $C^{\alpha}_{n\ell m}$ and $D^{\alpha}_{n\ell m}$, are easily eliminated. This circumstance, on one hand clarifies the inessentiality of the symmetrization of the internal field, and on the other hand yields, for each ν, p, r_{α} a system involving only the A's and B's as unknowns:

$$\sum_{\tau}\sum_{\beta\in\tau}\sum_{L}\left\{\sum_{N}\sum_{M\in N}\left(\delta_{L\ell}\delta_{Mm}\delta_{\sigma\beta}\left[R^{\beta}_{L}\right]^{-1} + H^{\alpha\beta}_{\ell m LM}\right)a^{\nu p\beta}_{NLM} A^{\nu p\beta}_{NL} + \sum_{N'}\sum_{\bar{M}\in N'} K^{\alpha\beta}_{\ell m L\bar{M}}\, b^{\nu p\beta}_{N'L\bar{M}} B^{\nu p\tau}_{\eta N'L}\right\}$$

$$= -\sum_{LM}\sum_{M'} W_{\eta LM}(\hat{k})\left[\eta c^{\nu p}_{LMM'} L^{\alpha}_{\ell m LM'} + d^{\mu p}_{LMM'} J^{\alpha}_{\ell m LM'}\right] \tag{4-4a}$$

$$\sum_{\tau}\sum_{\beta\in\tau}\sum_{L}\left\{\sum_{N'}\sum_{\bar{M}\in N'}\left(\delta_{L\ell}\delta_{Mm}\delta_{\sigma\beta}\left[S^{\beta}_{L}\right]^{-1} + H^{\alpha\beta}_{\ell m L\bar{M}}\right)b^{\nu p\beta}_{N'L\bar{M}} B^{\nu p\beta}_{\eta N'L} + \sum_{N}\sum_{M\in N} K^{\alpha\beta}_{\ell m LM}\, a^{\nu p\beta}_{NLM} A^{\nu p\tau}_{\eta NL}\right\}$$

$$= -\sum_{LM}\sum_{M'} W_{\eta LM}(\hat{k})\left[c^{\nu p}_{LMM'} L^{\alpha}_{\ell m LM'} + \eta d^{\mu p}_{LMM'} J^{\alpha}_{\ell m LM'}\right] \tag{4-4b}$$

where we define

$$R_\ell^\alpha = \left[\frac{j_\ell(kr_\alpha)\frac{d}{dr_\alpha}(r_\alpha R_\ell^\alpha) - R_\ell^\alpha\frac{d}{dr_\alpha}(r_\alpha j_\ell(kr_\alpha))}{h_\ell(kr_\alpha)\frac{d}{dr_\alpha}(r_\alpha R_\ell^\alpha) - R_\ell^\alpha\frac{d}{dr_\alpha}(r_\alpha j_\ell(kr_\alpha))}\right]_{r_\alpha = b_\alpha} \tag{4-5a}$$

$$S_\ell^\alpha = \left[\frac{j_\ell(kr_\alpha)\frac{d}{dr_\alpha}(r_\alpha S_\ell^\alpha) - n_\alpha^2 S_\ell^\alpha\frac{d}{dr_\alpha}(r_\alpha j_\ell(kr_\alpha))}{h_\ell(kr_\alpha)\frac{d}{dr_\alpha}(r_\alpha S_\ell^\alpha) - n_\alpha^2 S_\ell^\alpha\frac{d}{dr_\alpha}(r_\alpha h_\ell(kr_\alpha))}\right]_{r_\alpha = b_\alpha} \tag{4-5b}$$

Since the spheres within a set are identical to each other, R_ℓ^α and S_ℓ^α do not actually depend on α but only on the set index, σ. Therefore, from now on these quantities will be indicated by R_ℓ^σ and S_ℓ^σ, respectively. Equation (4-4) can be put in a more symmetrical form through the use of equation (3-6). Indeed, multiplication of equation (4-4a) by $(a_{n\ell m}^{\nu p d})^*$, and of equation (4-4b) by $(b_{n\ell m}^{\nu p d})^*$, and summation over the α's belonging to the σ-th set and over m yield for each ν, p, τ the equations

$$\sum_s \delta_{rs}\left[R_s\right]^{-1} + H_{rs}^{\nu}(m)\, A_{ns}^{\nu p} + \sum_{s'} K_{rs'}^{\nu}(m,e)\, B_{ns'}^{\nu p} = -P_{nr}^{\nu p} \tag{4-7a}$$

$$\sum_{s'}\left(\delta_{r's'}\left[S_{s'}\right]^{-1} + H_{r's'}^{\nu}(e)\right) B_{ns'}^{\nu p} + \sum_s K_{r's}^{\nu}(e,m)\, A_{ns}^{\nu p} = -Q_{ns'}^{\nu p} \tag{4-7b}$$

In equation (4-7) we put, for the sake of simplicity,

$$r \equiv (\sigma,\ell,n),\ s \equiv (\tau,L,N),\ r' \equiv (\sigma,\ell,n'),\ s' \equiv (\tau,L,N')$$

and define

$$H_{rs}^{\nu}(m) = \sum_{\alpha m}\sum_{\beta M}(a_{n\ell m}^{\nu p\alpha})^* H_{\ell mLM}^{\alpha\beta}\, a_{NLM}^{\nu p\beta} \tag{4-8}$$

$$K_{rs}^{\nu}(m,e) = \sum_{\alpha m}\sum_{\beta M}(a_{n\ell m}^{\nu p\alpha})^* K_{\ell mLM}^{\alpha\beta}\, b_{NLM}^{\nu p\beta} \tag{4-9}$$

with an obvious meaning of the parameters e, m. The quantities $H_{rs}^{\nu}(e)$ and $K_{rs}^{\nu}(m,e)$ are identical to $H_{rs}^{\nu}(m)$ and $K_{rs}^{\nu}(e,m)$ respectively, except for the mutual exchange of the a's with the b's.
Moreover

$$P_{nr}^{\nu p} \sum_{LM}\sum_{\alpha m}\sum_{M'} W_{nLM}(\hat{k})\left[n c_{LMM'}^{\nu p}\, L_{\ell mLM'}^{\alpha} + d_{LMM'}^{\nu p}\, J_{\ell mLM'}^{\alpha}\right]\left(a_{n\ell m}^{\nu p\alpha}\right)^*$$

$$Q_{nr}^{\nu p} = \sum_{LM}\sum_{\alpha m}\sum_{M'} W_{nLM}(\hat{k})\left[c_{LMM'}^{\nu p}\, L_{\ell mLM'}^{\alpha} + n d_{LMM'}^{\nu p}\, J_{\ell mLM'}^{\alpha}\right]\left(b_{n\ell m}^{\nu p\alpha}\right)^*$$

We remark that in equations (4-7) and (4-8) the superscript p on

$\tilde{H}$ and $\tilde{K}$ is missing. As will be shown later, these quantities are actually independent of the row index so that p has been dropped.

5. THE CROSS SECTIONS

Once the coefficients $A_n^{\nu p\sigma}$ and $B_n^{\nu p\sigma}$ are known, all the scattering properties of the cluster can easily be calculated. For this purpose, symmetry is not essential and we can revert to the unsymmetrized expansion of the scattered field through equation (3-6). It is convenient to express the scattered field in terms of vector harmonics centered at a single point through the addition theorem already used in the preceding section.[18] If $\underset{\sim}{R}_o$ is the vector position of the chosen point and $\underset{\sim}{r}_o = \underset{\sim}{r} - \underset{\sim}{R}_o$

$$\underset{\sim}{E}_n^{(s)} = \sum_\alpha \sum_{LM} \Big\{ A^\alpha_{nLM} \sum_{L'M'} \Big[\mathcal{J}^{0\alpha}_{L'M'LM}\, h_{L'}(kr_0)\underset{\sim}{X}_{L'M'}(\hat{r}_0) + \mathcal{L}^{0\alpha}_{L'M'LM} \frac{1}{k}\nabla\times h_{L'}(kr_0)\underset{\sim}{X}_{L'M'}(\hat{r}_0) \Big]$$

$$+ B^\alpha_{nLM} \sum_{L'M'} \Big[\mathcal{L}^{0\alpha}_{L'M'LM}\, h_{L'}(kr_0)\underset{\sim}{X}_{L'M'}(\hat{r}_0) + \mathcal{J}^{0\alpha}_{L'M'LM} \frac{1}{k}\nabla\times h_{L'}(kr_0)\underset{\sim}{X}_{L'M'}(\hat{r}_0) \Big] \Big\}$$

$$= \sum_{L'M'} \Big\{ \tilde{A}_{nL'M'}\, h_{L'}(kr_0)\underset{\sim}{X}_{L'M'}(\hat{r}_0) + \tilde{B}_{nL'M'} \frac{1}{k}\nabla\times h_{L'}(kr_0)\underset{\sim}{X}_{L'M'}(\hat{r}_0) \Big\} \qquad (5\text{-}1)$$

and an analogous expression for $i\underset{\sim}{B}_n^{(s)}$ with

$$\tilde{A}_{nL'M'} = \sum_\alpha \sum_{LM} \Big[A^\alpha_{nLM} \mathcal{J}^{0\alpha}_{L'M'LM} + B^\alpha_{nLM} \mathcal{L}^{0\alpha}_{L'M'LM} \Big] \qquad (5\text{-}2a)$$

$$\tilde{B}_{nL'M'} = \sum_\alpha \sum_{LM} \Big[A^\alpha_{nLM} \mathcal{L}^{0\alpha}_{L'M'LM} + B^\alpha_{nLM} \mathcal{J}^{0\alpha}_{L'M'LM} \Big] \qquad (5\text{-}2b)$$

$\mathcal{J}^{o\alpha}_{L'M'LM}$ and $\mathcal{L}^{o\alpha}_{L'M'LM}$ are given by equation (4-3) but for the substitution of j_λ to h_λ. Equation (5-1) is valid provided that $r_o > R_{o\alpha} = |\underset{\sim}{R}_\alpha - \underset{\sim}{R}_o|$, i.e., in the region outside a sphere centered at $\underset{\sim}{R}_o$ and including the whole cluster. Therefore choosing $\underset{\sim}{R}_o = 0$ and thus letting the center of the expansion (5-1) coincide with the center of symmetry of the cluster, the radius of the above sphere is minimized. Anyway the coefficients $\underset{\sim}{A}$ and $\underset{\sim}{B}$, unlike those of the field scattered by a single sphere, depend on the direction of the incident wavevector, $\underset{\sim}{k}$. As a consequence all the quantities of interest depend both on $\underset{\sim}{k}$ and on the scattered wavevector, $\underset{\sim}{k}_s = k\underset{\sim}{r}$, except, of course, the scattering, absorbtion and total cross-sections which depend only on $\underset{\sim}{k}$. A straightforward calculation shows, in fact, that

$$\sigma_n^{(s)} = \frac{2\pi^2}{k^2} \sum_{L'M'} \Big\{ |\tilde{A}_{nL'M'}|^2 + |\tilde{B}_{nL'M'}|^2 \Big\} \qquad (5\text{-}3a)$$

$$\sigma_n^{(abs)} = \frac{2\pi^2}{k^2} \sum_{L'M'} \left\{ 2|W_{nL'M'}|^2 - |\tilde{A}_{nL'M'} + W_{nL'M'}|^2 - |\tilde{B}_{nL'M'} + W_{nL'M'}|^2 \right\} \quad (5\text{-}3b)$$

$$\sigma_n^{(tot)} = \frac{4\pi^2}{k^2} \sum_{L'M'} \mathrm{Re}\left\{ W^*_{nL'M'} (\tilde{A}_{nL'M'} + \tilde{B}_{nL'M'}) \right\} \quad (5\text{-}3c)$$

Finally, we notice that the cross sections depend on the polarization of the incident wave, η, as explicitly indicated in equation (5-3).

6. DISCUSSION

In the preceding sections we used group theory to put the system for the coefficients of the scattered wave in factorized form. Let us now rewrite equation (4-7) matrixwise as

$$\begin{vmatrix} \underset{\sim}{R}^{-1} + \underset{\sim}{H}^{\nu}(m) & \underset{\sim}{K}^{\nu}(m,e) \\ \underset{\sim}{K}^{\nu}(e,m) & \underset{\sim}{S}^{-1} + \underset{\sim}{H}^{\nu}(e) \end{vmatrix} \begin{vmatrix} A^{\nu p} \\ B^{\nu p} \end{vmatrix} = \begin{vmatrix} P^{\nu p} \\ Q^{\nu p} \end{vmatrix} \quad (6\text{-}1)$$

in self explanatory notation. Clearly the dependence on p of the right-hand side of equation (6-1) forces us to solve all the systems arising from the factorization procedure. Nevertheless, the matrix on the left-hand side of equation (6-1) does not depend on p, just as in the case of a secular problem. The p-independence of R and S , indeed, follows from their very definition, equation (4-5). These quantities occur even in the theory of electromagnetic scattering from a single sphere[20] and are the electromagnetic analog of the elements of the transition-matrix in quantum scattering theory.[21] H^{ν} and K^{ν} , in turn are the symmetrized counterparts of and , equation (4-3), which are the matrix elements in the site and angular momentum representation of G, the dyadic Green's function for free space propagation of spherical vector waves. The p-independence of H and K is then a direct consequence of the invariance of $\underset{\sim}{G}$ under the symmetry operations. Therefore, the matrix on the left of equation (6-1), which can be interpreted as the inverse of the transition matrix for the whole cluster,[22] turns out to be independent of p. This circumstance greatly reduces the computational work in the case of multidimensional irreducible representations. Anyway the computational work needed to solve our scattering problem depends on the number of spheres in the cluster and on the number of L-values included in the expansion of the scattered field, equation (2-3) or (3-5). For a cluster of N spheres and including multipoles up to the order L_M, the dimension of the unsymmetrized system is $d = 2N(L_M + 1)^2 - 2N$, while if group theory is used, the order of the factorized systems depends on the group of the cluster. As an example let us consider a cluster of 5 spheres with point group T_d (the SO_4^{--}, CH_4 molecules have just this structure). Table 1 shows the order of the symmetrized systems and that of the unsymmetrized one for values of L up to 4. Anyway, from the work

of Mie[23] and of Debye[24] we know that, for a sphere of radius, b, $L_M = 1$ is quite sufficient for a good description of the scattered field, provided that Kb << 1. Now, since our cluster is meant to modellize a molecule, the radius of the spheres can hardly exceed 3 Å so that in the visible and infrared range $Kb_\alpha < 10^{-3}$ for any α. Therefore, even allowing for the effect of multiple-scatterings, $L_M = 3$ should be quite sufficient to achieve fairly converged values of the scattered field.

Table 1

L_M	1	2	3	4
A_1	1	2	6	10
A_2	1	2	6	10
E	2	8	12	20
F_1	4	10	19	30
F_2	4	10	19	30
U	30	80	150	240

Dimension of the symmetrized and unsymmetrized systems for L_M up to 4 for a cluster of 5 spheres with a point group Td. The entry U means unsymmetrized while the other entries indicate the irreducible representations in the notation of Hamermesh.[15]

7. COMPUTER CODES

The method described has been implemented through computer algorithms whose practical application we briefly describe. The first code has a main program named SYMULT and subroutines PRMUTE, PRJECT, FUNCTION DL, PRJPW, ORTHOG. The second main program, named MUSCA, has subroutines RESYCO, REPAPW, GHMT, GJMT, CHGK, GIGL, SHMME, SKMME, SPQ, MULAM, CROSSE, CMES, ZOTS, WLM, RSINV, AUXIL, FUNCTION DCLEB, RBF, RNF, CBF, POLAR, SPHAR, DCMLIN, COMPLEX FUNCTION DCDOT.

SYMULT only reads the input data and calls the subroutines, which actually perform the mathematical computations, and finally prints the output, which consists of the following quantities:

1. Names of the operations for the group, , with the corresponding parameters: ω , angle of rotation, λ , μ, ν direction cosines; and the permutations induced on the sites of a given set by the operations of . For the operations of group and associated operator ecc we refer to eqs. (3-2a) (3-2b) and following explanations.

2. Coefficients of the independent combinations of magnetic and electric multipoles centered at the sites of the given set, such quantities are computed from eqs. (3-4a), (3-4b).

3. The projections of the magnetic and electric multipoles included in the expansion of the incident plane wave, as are shown in eqs (3-9).

These quantities are written on a file and are the input data for MUSCA, whose output consists of the following quantities:

1. The total cross section, computed from eq (3-5c)
2. The scattering cross section, from eq (3-5a)
3. The absorption cross section, from eq (3-5b)
4. The coefficients of the scattered wave for each representation, the $A_{nNL}^{\nu p\sigma}$ and $B_{nNL}^{\nu p\sigma}$ of eq (3-6), which are the unknown quantities in our solution and thus, with their knowledge we are able to fully describe the properties of the cluster, as stated in section 5.

Following are some data obtained from these programs (outputs of SYMULT and MUSCA) for the case of the point group Td (SO_4^{--}) and comparison is made with experimental data.

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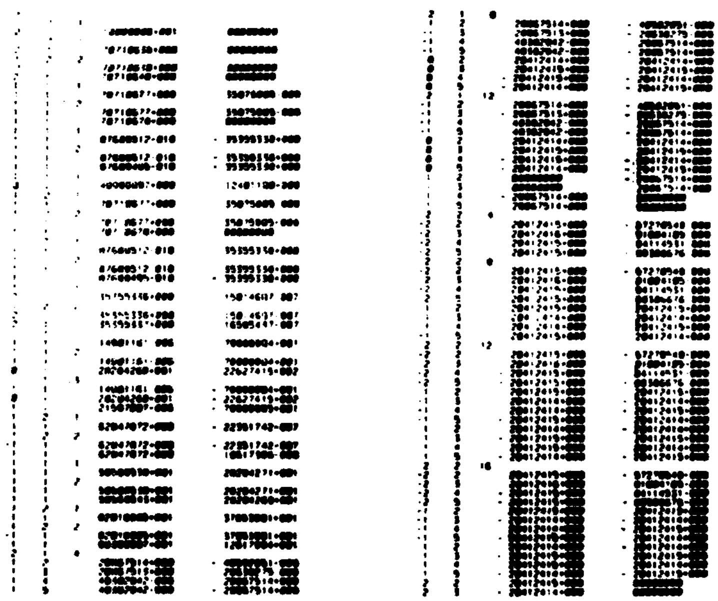
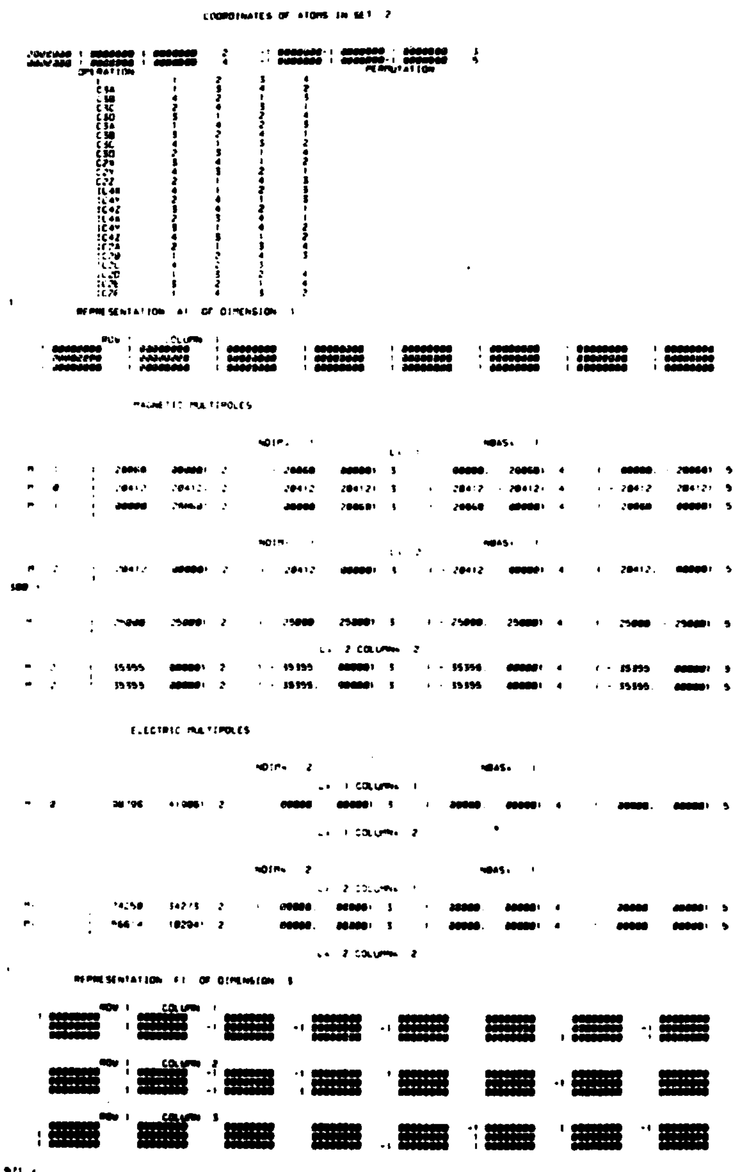
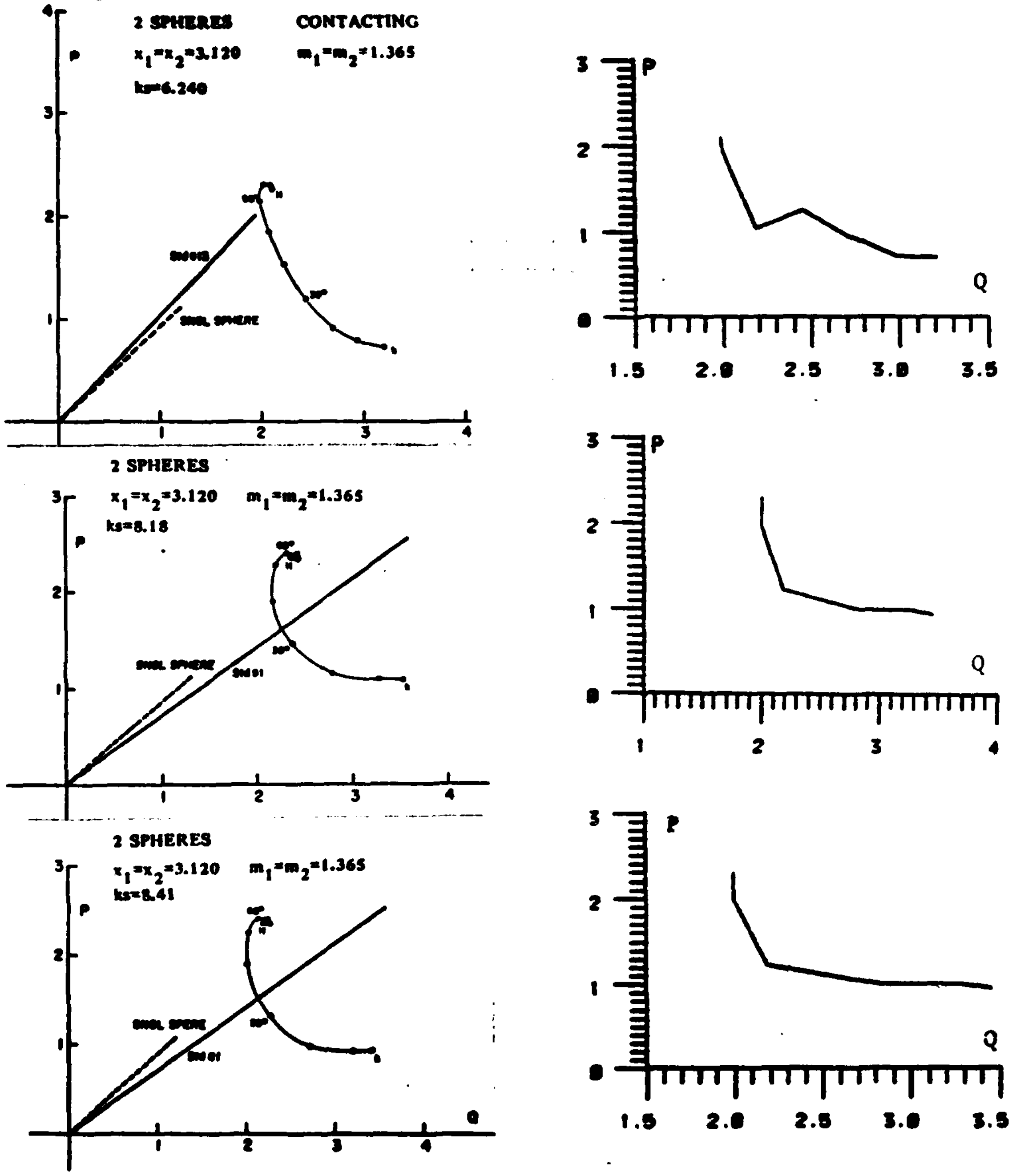


sample output from Musca



sample output from Symult

Experimental Results [29,30] Computed Results



Comparison of experimental and computed results for P=*Im[σ(θ)]* and Q=*Re[σ(θ)]* with θ=0

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